RESEARCH ARTICLE

EFFECT OF TEMPERATURE ON OPTICAL PROPERTIES OF NANOCRYSTALLINE CERAMICS Fe₂Mn₂Ni₂Zn₂O₁₁

*,[1]Anitha S Nair, [2]Vinila, V. S. and [2]Jayakumari Isac

[1]Department of Physics, D. B. College, Parumala, Pathanamthitta, India
[2]Department of Physics, CMS College, Kottayam, India

ABSTRACT

In this article the effect of temperature on optical properties of nano crystalline ceramic Ferromanganese nickel zinc oxide Fe₂Mn₂Ni₂Zn₂O₁₁ were studied. Using the Tauc model, the absorption spectrum method was applied to estimate the optical band gap. The sample was synthesized thermo chemically by solid state method at different treating temperatures. A characteristic feature of all solid-state reactions is that they involve the formation of product phase(s) at the interfaces of the reactants. UV-VIS analysis of the sample was carried out. The optical constants of refractive index, extinction coefficient, normal-incidence reflectivity, and absorption coefficient showed systematic variation with temperature. From these data the absorption coefficient was calculated and the band gap energy determined. Using the Wemple- Di Domenico single-oscillator model the dispersion of refractive index was analyzed.

Citation: Anitha S Nair, Vinila, V. S. and Jayakumari Isac, 2016. "Effect of temperature on optical properties of nanocrystalline ceramics Fe₂Mn₂Ni₂Zn₂O₁₁", *International Journal of Current Research*, 8, (11), 40976-40981.

INTRODUCTION

Optical gap is different from the quasi-particle gap (at least in the conventional BCS theory for bulk materials, the superconducting gap coincides with the quasi-particle gap arising from paring). In optical experiments (Tauc plot is used for determining optical gap) one excites particles that remain to interact with the hole they leave behind; in contrast, in photo-emission (and inverse photo-emission) experiments, one truly removes (adds) particles from (to) systems. The optical gap is in general smaller than the quasi-particle gap, the difference being the binding energy of the bound states that electrons can form with holes (forming excitons). This binding energy can be small, whereby optical gap can be very close to the quasi-particle gap, but this is not in general the case. Incidentally, because bound states cannot be calculated by means of finite-order perturbation theory, calculation of the optical gap in general requires solving the relatively complicated Bethe-Salpeter equations (www.scholarpedia.org/article/Bethe-Salpeter_equation_(origins)). In the present work the authors describes the optical behaviour of Fe₂Mn₂Ni₂Zn₂O₁₁ a nano crystalline ceramic material.

*Corresponding author: Anitha S Nair,
Department of Physics, D. B. College, Parumala, Pathanamthitta, India.

The energy band gap values of the sample were analyzed for different temperatures and they are fundamentally important to the design of practical devices (Nepal *et al*., 2005). In solid-state physics, a band gap, also called an energy gap, is an energy range in a solid where no electron states can exist. In graphs of the electronic band structure of solids, the band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material, so the band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps or none, because the valence and conduction bands overlap (Band gap From Wikipedia the free encyclopedia). Measuring the band gap is an important factor in determining the electrical conductivity in nano material industries. A Tauc plot is used to determine the optical gap, or Tauc gap, in semiconductors. The Tauc gap is often used to characterize practical optical properties of amorphous materials (Tauc plot From Wikipedia, the free encyclopedia). The band gap energy values obtained using Tauc plot showed a

direct relation with temperature. The optical constants of refractive index, extinction coefficient, and absorption coefficient showed a systematic variation with temperature. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model and such optical behaviour is rarely reported. The Urbach energy of the sample was also studied.

Experimental

Nanocrystalline ceramics with the chemical formula $Fe_2Mn_2Ni_2Zn_2O_{11}$ was prepared by the solid state reaction technique according to the molecular formula. The powders of the required ceramics were mixed mechanically, ball milled and then attrition milled. Manganese oxide, nickel oxide, zinc oxide, ferric oxide powders were used as the raw materials (Anitha *et al.*, 2014). Then the material was calcined at different treating temperatures, 30^0C, 500^0C, 800^0C and 950^0C. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size (Vinila *et al.*, 2014). Then UV-Vis spectrum of these materials was taken. The dispersion of refractive index was analyzed by the Wemple- Di Domenico single-oscillator model. The optical constants of refractive index, extinction coefficient, normal-incidence reflectivity, and absorption coefficient showed systematic variation with temperature.

UV-VIS. Analysis

UV–Vis spectroscopy was used to characterize the optical absorption properties (Kumar *et al.*, 2013). The optical absorption spectrum of the sample were studied at room temperature. The optical absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors (Dhannia *et al.*, 2009 and Varghese *et al.*, 2002). The UV–vis absorption spectra of the samples were recorded in the wavelength range of 200 to 800 nm using a Shimadzu UV 3600 UV–vis-NIR spectrometer (Shimadzu Corporation, Kyoto, Japan) in diffuse reflectance mode. Spectra were recorded at room temperature, and the data were transformed through the Kubelka-Munk function (Kumar, 2013). This type of sample has high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environment. UV-Visible spectrum gave information about the excitonic and inter transition of nano materials (Choudhury *et al.*, 2013) Figure.1 shows the UV-VIS behaviour of the sample $Fe_2Mn_2Ni_2Zn_2O_{11}$ at 950^0C.

The diffuse reflectance spectra were translated into the absorption spectra by the Kubelka-Munk method. Kubelka-Munk's equation is described as follows:

$\alpha = (1-R)^2/2R$ - (1), where α is the absorption coefficient and R the reflectivity at a particular wavelength (Keigo Suzuki *et al.*, 2005). A Tauc plot is a convenient way of displaying the optical absorption spectrum of a material, pioneered by Jan Tauc (/taʊts/), who proved that momentum is not conserved even in a direct optical transition. Typically, a Tauc plot shows the quantity hυ (the energy of the light) on the abscissa and the quantity $(\alpha h\upsilon)^{1/r}$ on the ordinate, where α is the absorption coefficient of the material. The value of the exponent r denotes the nature of the transition: r = 1/2 for direct allowed transitions r = 3/2 for direct forbidden transitions r = 2 for indirect allowed transitions r = 3 for indirect forbidden transitions. The resulting plot has a distinct linear regime

which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical band gap of the material (Tauc plot From Wikipedia, the free encyclopedia) According to the Tauc relation, the absorption coefficient α for a material is given by

$$\alpha = A(h\upsilon - E_g)^n \qquad\qquad\qquad \text{--(2)}$$

Where E_g the band gap, constant A is different for different transitions, (hv) is energy of photon in eV and n denotes the nature of the sample transition (Tauc *et al.*, 1968). Optical absorption and luminescence occur by transition of electrons and holes between electronic states (bands, tail states, gap states). If electron-phonon coupling is strong enough self-trapping occurs. Absorption coefficient α is defined by $I(z) = I_o \exp\{-\alpha z\}$. Where I(z) is the flux density if incident light is I_o, z is the distance measured from the incident surface. Hence $\alpha = -(1/I(z))\, dI(z)/dz$. Different regions of Tauc plot based on optical analysis can be presented as 3 regions: A region: The absorption coefficient, α, due to interband transition near the band-gap is well described: $\alpha\hbar\omega = B(\hbar\omega - Eg)^2$ $\hbar\omega$ is photon energy, Eg is optical bandgap. This Tauc plot defines the optical gap in amorphous semiconductors.
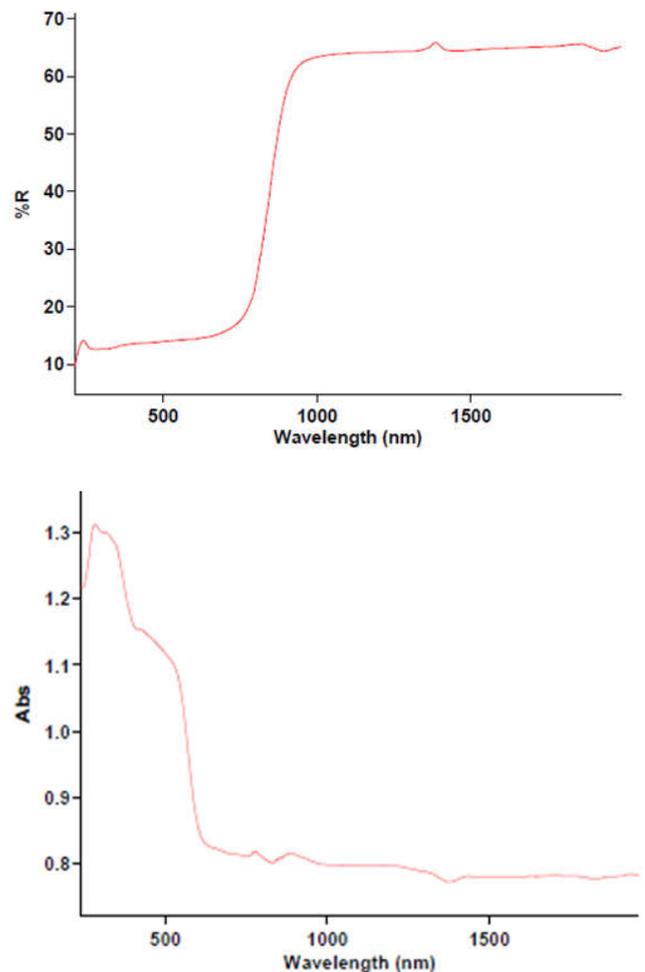
Figure 1. UV-VIS spectrum of $Fe_2Mn_2Ni_2Zn_2O_{11}$ (reflectance & absorbance)

B region: The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon energy $\alpha(\hbar\omega) \sim \exp(\hbar\omega/E_u)$, where E_u is called Urbach energy.

C region: In addition, optical absorption by defects also appears at energy lower than optical gap. Likewise α is written as another exponential function of photon energy: $\alpha(\hbar\omega) \sim \exp(\hbar\omega/E_d)$, E_d belongs to the width of the defect states. C region is rather sensitive to the structural properties of materials (Kugler, 2014). The edge arises due to a radiative recombination between trapped electrons and trapped holes in tail and gap states as shown in Fig.2 and is dependent on the degree of structural and thermal disorder (Dennis *et al.*, 2014). The tauc plot of the sample is given in Fig 5. It is reported that optical gap energy of nano –sized crystal depends on its crystallite size, it increases with decreasing crystallite size in the nano size range (Lu *et al.*, 1996 and Golego *et al.*, 1998). The extinction coefficient and the absorption coefficient are related as

$$\alpha(E) = 4\pi/\lambda \; (k(E)) \qquad\qquad ---(3).$$

Variation of band gap energy with samples annealed at different temperatures is shown in Figure 4. The natural logarithm of the absorption coefficient, $\alpha(\nu)$, was plotted as a function of the photon energy, $h\nu$ (Fig.7). The value of Eu was calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of curves. The measurement of temperature-dependent Urbach tails distinguishes a temperature-dependent tail and a temperature-independent part, which mainly are due to intrinsic defects. The latter can be controlled by improving the crystal growth and the purity of the ingredients. The temperature-dependent part of the Urbach tail, is purely of intrinsic reasons (Letz *et al.*, 2010).
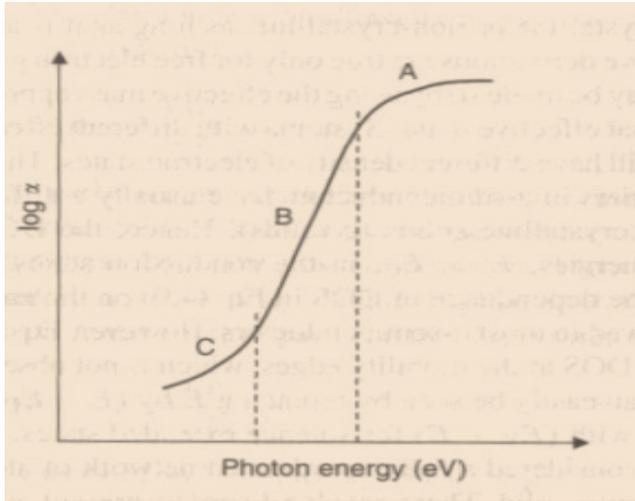
Fig. 2. Optical band gap energy variation with absorption

The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon energy:

$$\alpha(\hbar\nu) \sim \exp(\hbar\nu/E_u) \qquad\qquad --(4)$$

where E_u is called Urbach energy. The region B in the Fig.2 represents the Urbach energy. The absorption edge called the Urbach energy, depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies (Sumi *et al.*, 1971 and Kugler *et al.*, 2013). It is observed in many cases that optical absorption by defects also appears at energy lower than optical gap (region C of Fig. 2). This region is related to the structural

properties of materials (Tariq *et al.*, 2010). Fig.3 shows the typical tauc plot calculation.
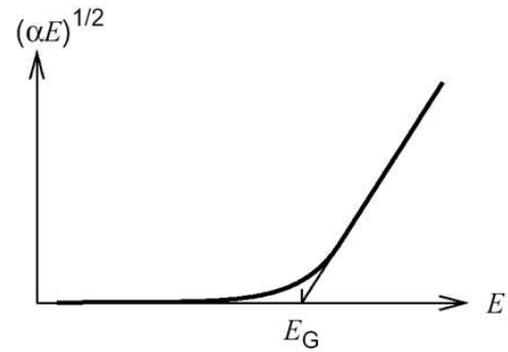
Fig. 3. Tauc plot

Refractive Index and Dispersion

There is a change in refractive index with wavelength. The refractive index values show a linear decrease with the increase in wavelength,Fig.7 shows the variation of the dispersion curve with annealing temperatures.The refractive index dispersion of the thin film is expressed as equation of Didomenico as $n^2 -1 = E_d E_0/(E_d^2 - (h\nu)^2) - (5)$ where n is the refractive index, h is Planck's constant, ν is the frequency, $h\nu$ is the photon energy, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is the measure of the strength of interband optical transitions. The dielectric response for transitions below the optical gap is described by this model. E_o and E_d values were calculated from the slope and intercept on the vertical axis of plot of $1/(n^2 - 1)$ versus $(h\nu)^2$ (DiDomenico, 1968, 1969). The static refractive index n(0) at zero photon energy is evaluated from Equation (5), i.e. $n_2(0) = 1 + E_d/E_o - (6)$ (Reenu Jacob *et al.*, 2014). The dependence of extinction coefficient (k) on the wavelength is shown in Figure 4. The Figure shows an increase in k value with increasing wavelength.
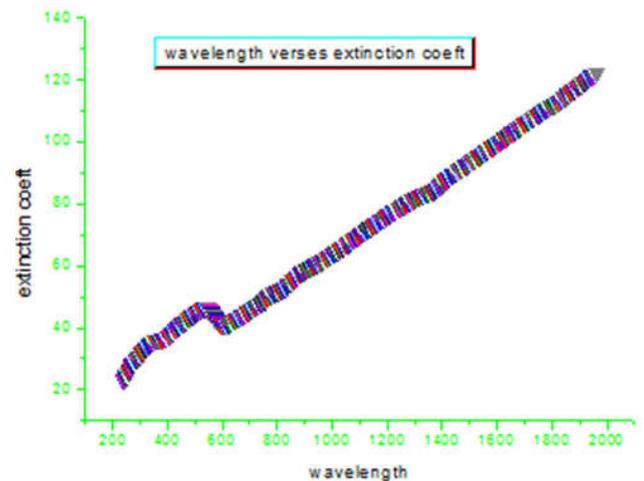
Fig. 4. Extinction coefficient varies with wavelength

The extinction coefficient can be calculated by the relation $k = \alpha \lambda/4\pi$ …Where λ is the wavelength, α is the absorption coefficient. The refractive index of the films was calculated by the following equation $n = \{(4R/(R-1)^2 - K2) - (R-1)/(R-1)\}^{1/2}$ where R the reflectance and k the extinction coefficient (Wug-

Dong Park *et al*., 2012). Refractive index value shows a slight increase with increasing annealing temperature and attains a fixed value after a particular wavelength. The refractive index values showed a linear decrease with the increase in wavelength when plotted with refractive index along the Y-axis and wavelength along the X axis (Figure 8).

RESULTS AND DISCUSSION

The optical analysis of the ceramic material prepared by solid state reaction technique and treated at different temperatures was successfully done using UV-Vis Spectrophotometer. UV-VIS analysis, clearly confirms that band gap energy of the nano ceramic increases as the annealing temperature of the sample is increased. Here the direct allowed transitions are considered. The calculated values of the band gap energy of the sample at different values of temperature is given in Table -1. The Tauc plot is plotted with hv along the X-axis and $(hv\alpha)^2$ along the Y-axis. The band gap at a particular temperature is found by extrapolating the X axis. The Tauc plot of the sample at temperatures 950^0C is given in Fig.5.
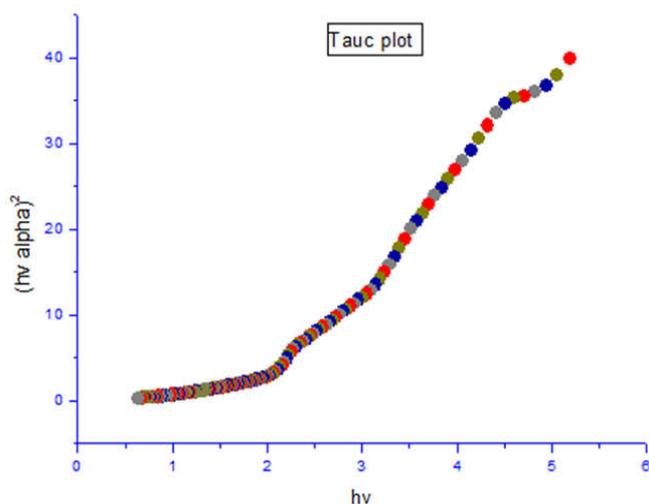
Fig. 5. The Tauc plot of $Fe_2Mn_2Ni_2Zn_2O_{11}$

Table 1. Band gap energy values of $Fe_2Mn_2Ni_2Zn_2O_{11}$ at different temperatures

Temperature	Band gap energy in eV
30∘C	1.28
500∘C	1.34
800∘C	1.71
950∘C	2.24

Fig.6 shows the variation of band gap energy with increase in annealing temperature. The energy levels are dependent on the degree of structural order–disorder in the lattice. The band gap increases with the crystallite size but decreases as the perosvkite phase is formed which proves the quantum confinement also decreasing its dislocation density.

Due to an increase in temperaturethe crystallite size also increases which shows an increase in band gap energy (Reenu Jacob *et al*., 2014). The energy levels are dependent on the degree of structural order–disorder in the lattice. Therefore, the increase of structural organization in nano ceramic leads to a reduction of the intermediatery energy levels and consequently increases the E_g values. Tauc plot data well confirms that the band gap energy of the sample increases slightly when the

temperature is increased. A graph is drawn with natural logarithm of the absorption coefficient against energy in eV (Figure 7). Urbach energy is calculated from this. This value is found to be lower than the band gap energy and hence Sumi-Toyozawa (ST) model theory can be well applied to this material.
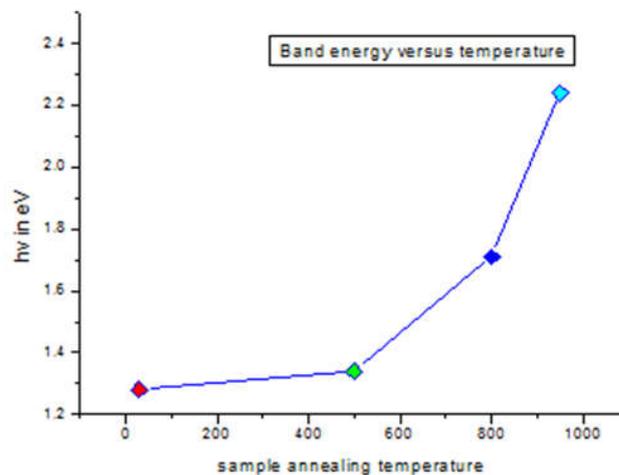
Fig.6. Band gap energy variation with the samples at varied annealing temperature *of* $Fe_2Mn_2Ni_2Zn_2O_{11}$
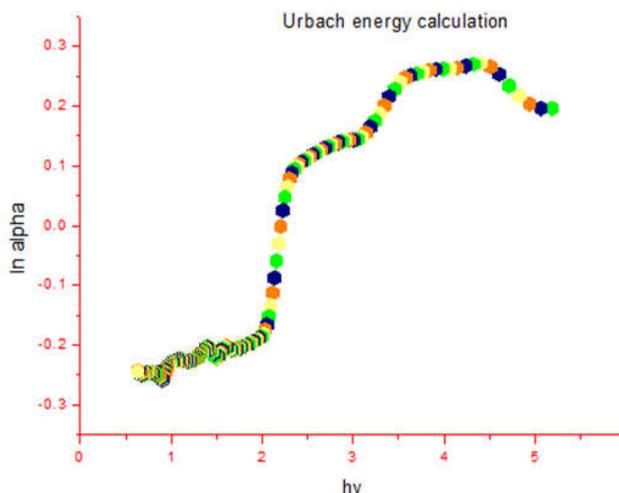
By the study of the variation of refractive index of the sample at different values of temperature it is analyzed that refractive index of the sample decreases as the wavelength increases and attains a definite value at all temperatures. This linear variation of the refractive index with the wavelength is due to dispersion of light energy at the different interstitial layers. The refractive index of perovskites is known to be proportional to their electronic polarization per unit volume which is inversely proportional to distance between. The refractive index also shows a linear relation with the photon energy (Fig. 8). The increase in refractive index is due to crystallization of the perovskite phase. This result can also be explained by an increase in crystallite size. The dispersion energy of the sample is calculated using the Wemple-DiDomenico (WD) model. Results are plotted graphically in (Fig.8). Refractive index of the sample annealed at different temperatures can be calculated using Sellmeir dispersion formula (DiDomenico and Wimple, 1968, 1969).

Plotting of $(n^2-1)^{-1}$ against $(h\,v)^2$ allows to determine, the oscillator parameters, by fitting a linear function to the smaller

energy data, E_o and E_d can be determined from the intercept, (E_o/E_d) and the slope $(1/E_oE_d)$. Eo is considered as an average energy gap to, it varies in proportion to the Tauc gap $E_o\sim 2E_g$. The data of the dispersion of the refractive index (n) were evaluated according to the single oscillator model proposed by wimple and Di Domenico as, $n^2 = 1 + (E^dE^0)/(E_0^2 - hv^2)$ ----(7).
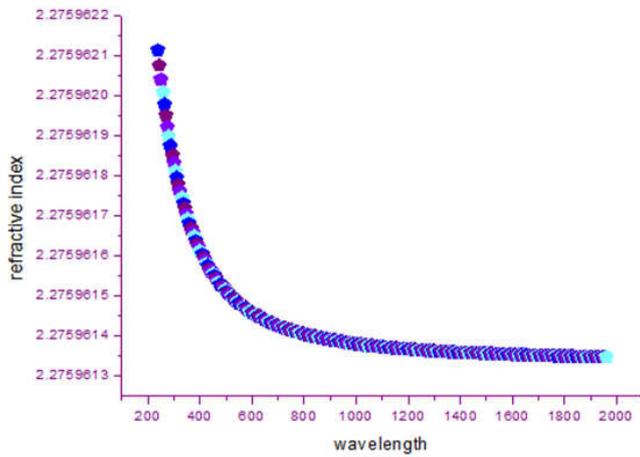
a
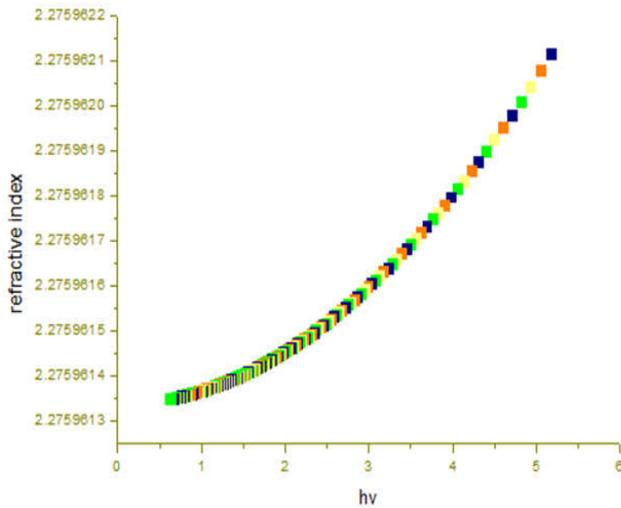
(b)

Fig. 8. Variation of Refractive index (n) with (a) wavelength and (b) photon energy of Fe$_2$Mn$_2$Ni$_2$Zn$_2$O$_{11}$
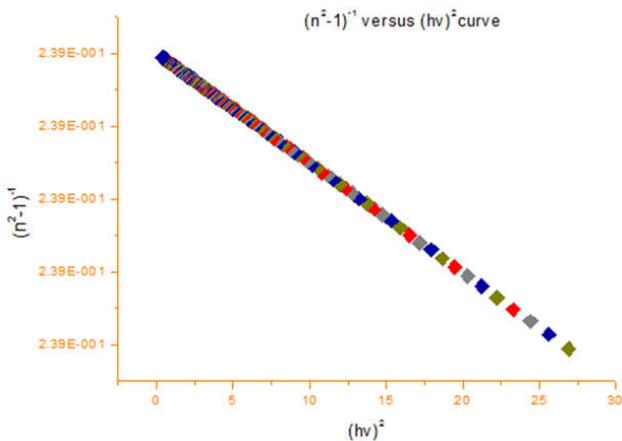
Fig. 9. (n^2-1)$^{-1}$ versus (hv)^2 curve

where E_o is the oscillator energy and E_d is the oscillator strength or dispersion energy. The curves of $(n^2-1)^{-1}$ against $(1/\lambda^2)$ (Fig.10) are fitted into straight lines following the sell Meier's dispersion formula. The value of So and (λ_o) are estimated from the slope $(1/S_o)$ and the infinite wavelength intercept $(1/S_0\lambda_o)^2$. The optical parameters of the sample were calculated and listed in the table 2 given below. The oscillator model can be also written as $n^2-1=S_0 \lambda_0^2 /(1-(\lambda_o / \lambda)^2)$--- (8) where λ is the wavelength of the incident radiation , S_o is the average oscillator strength and λ_o is an average oscillator wavelength. From the above table it is clear that as the temperature is increased, band gap energy E_g and the oscillator energy E_0 also increases. The dispersion energy also shows a decline as the temperature rises and the sample attains its perosvkite phase.
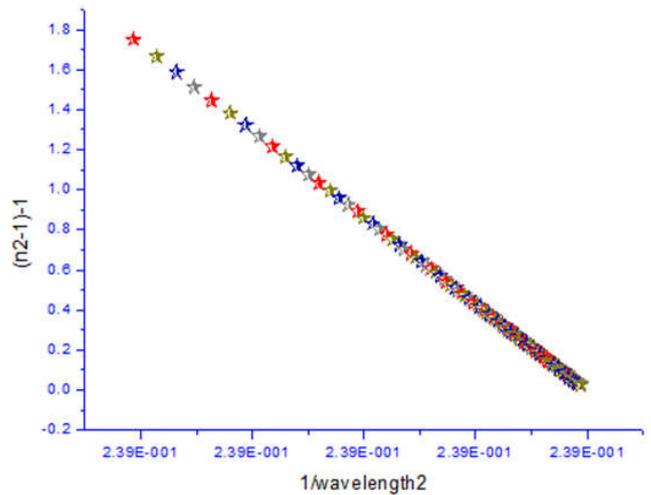
Fig.10. (n^2-1)-^{1} versus 1/ λ^2 curve

Table 2. The calculated values of the optical parameters of Fe$_2$Mn$_2$Ni$_2$Zn$_2$O$_{11}$

Sample	E_g(eV)	E_O(eV)
At 30^{0}C	1.28	2.56
At 500^0 C	1.71	3.42
At 800^0 C	2.24	4.48
At 950^0 C	2.34	4.68

Further the mechano chemical process has an advantage due to low-costs and widely available materials, leading to a simplified process. The curves with straight line graphs confirms the Sell Meier's dispersion formula.

Conclusion

The increase in the band gap energy   increases the dielectric properties of the material. The UV emission peak shifts significantly to higher wavelengths with increasing annealing temperatures. It is confirmed that band gaps obtained varies by varying annealing temperatures. Band gap energy and the optical properties of the nano ceramic material Fe$_2$Mn$_2$Ni$_2$Zn$_2$O$_{11}$ can be used for UV_VIS shielding applications. According to Wemple-DiDomenico single-oscillator model the dispersion energy decreases as the sample attains its perosvkite phase. At high temperature the band gap energy increases and becomes more dielectric. For new generation capacitors nano crystalline ceramics Fe$_2$Mn$_2$Ni$_2$Zn$_2$O$_{11}$ will prove as a future substitute. Optical measurements confirmed that absorbance and reflectance increases with temperature.

REFERENCES

Anitha S Nair *et al*. 2005. Nano Trends: A Journal of Nanotechnology and Its Applications Volume 16, Issue 3, ISSN: 0973-418X.

Band gap From Wikipedia the free encyclopedia

Choudhury *et al*. 2013. *International Nano Letters*, 3:25 doi:10.1186/2228-5326-3-25 licensee Springer

Dennis P. Shay -Development and characterization of high temperature, high energy density dielectric materials to establish routes towards power electronics capacitive devices- The Pennsylvania State University The Graduate School Department of Materials Science and Engineering May 2014.

Dhannia, T., S. Jayalekshmi, M. C. SanthoshKumar, T. PrasadaRao and A. Chandra Bose, 2009. Effect of Aluminium, Doping and Annealing on Structural and Optical Properties of Cerium Oxide Nanocrystals, *Journal of Physics and Chemistry of Solids*, 70 (11), 1443 - 1447.

DiDomenico, M.J. and S.H. Wimple, 1968. 1969. *J.Appl. Phy*. 40 919680 720.

Golego, N., S.A Studenikin, M. Cocivera, *Chem. Mater*, 10 (1998) 2000

Keigo Suzuki, And Kazunori Kijima, 2005. Optical Band Gap Of Barium Titanate Nanoparticles Prepared By Rf-Plasma Chemical Vapor Deposition, *Japanese Journal of Applied Physics*, Vol. 44, No. 4a, 2005, Pp. 2081–2082, The Japan Society of Applied Physics.

Kugler, S. Lectures on AmorphousSemiconductors-4 May 2013. www.slideserve.com/leo/optical-properties

Kugler, S. 2014. Lectures on Amorphous semiconductors

Kumar *et al*. 2013. International Nano Letters, 3:30

Letz, M., A. Gottwald, M. Richter, V. Liberman, and L. Parthier Schott AG. 2010. Temperature-dependent Urbach tail measurements of lutetium aluminum garnet single crystal-Research and Development, Hattenbergstr. 10, D-55014 Mainz, Germany Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, D-10587 Berlin, Germany Lincoln Laboratory, MIT, 244 Wood St., Lexington, Massachusetts 02420-9108, USA Schott Lithotec AG, Otto-Schott-Str. 13, D-07745 Jena, Germany-Physical review B 81, 155109 _2010.

Lu, X.M., J.S. Zhu, W.Y. Zang, G.Q. Ma, Y.N.Wang, 1996. Thin solid Films 274; 165.

Nepal, N., J. Li, M. L. Nakarmi, J. Y. Lin, and H. X. Jianga_ Temperature and compositional dependence of the energy band gapof AlGaN alloys Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601

Reenu Jacob, Harikrishnan G Nair, Jayakumari, 2014. Isac-Optical band gap analysis of nano-crystalline ceramic PbSrCaCuO, *Journal of Advances in Physics*, ISSN 2347-3487.

Sumi H. and Y. Toyozawa, 1971. *J. Phys. Soc. Jpn*. 31, 342

Tariq J. Alwan, *Malaysian Polymer Journal*, Vol. 5, No. 2, p 204-213, 2010

Tauc plot From Wikipedia, the free encyclopedia

Tauc, J., Menth, A., 1972. Non Cryst. Solids, 569; 8.

Varghese, S., M. Iype, E. J. Mathew and C. S. Menon, 2002. Determination of the Energy Band Gap of Thin Films of Cadmium Sulphide, Copper Phthalocyanine and Hybrid Cadmium Sulphide/Copper Phthalocyanine from Its Optical Studies, Materials Letters, 56 (6), 1078 - 1083.

Vinila, V.S., Jacob, R., Mony, A., Nair, H.G., Issac, S., Rajan, S., Nair, A.S. and Isac, J. 2014. XRD Studieson Nano Crystalline Ceramic Superconductor PbSrCaCuO at Different Treating Temperatures. Crystal Structure Theoryand Applications, 3, 1-9. http://dx.doi.org/10.4236/csta.2014

Wug-Dong Park--Optical Constants and Dispersion Parameters of CdS Th in Film Prepared by Chemical Bath Deposition Electronic Materials and Devices Laboratory, Department of Railroad Drive and Control, Dongyang University, Yeongju 750-711, Korea pISSN: 1229-7607 eISSN: 2092-7592.

www.scholarpedia.org/article/Bethe-Salpeter_equation_ (origins) Scholarpedia Nov 20, 2008

****